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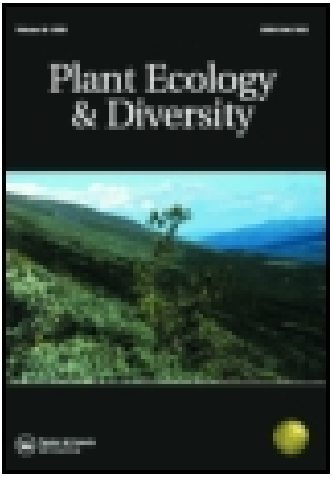

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George Wilson M.D.

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XXV. *On the presence of Fluorine in the Stems of Gramineæ, Equisetaceæ, and other Plants, with some Observations on the sources from which Vegetables derive this element.* By GEORGE WILSON, M.D.

READ 8TH JULY 1852.

THE author commenced by stating, that the earliest observer of the presence of fluorine in plants was Will of Giessen, who found traces of it in barley, the straw and grain of which were analysed together. The author reported to the Botanical Society, some four years ago, the results of his earlier researches into the distribution of this element throughout the vegetable kingdom, which were not very numerous or very encouraging. One reason of this was the small extent to which fluorine occurs in plants; another, and practically as serious a reason, was the difficulty of separating and recognising fluorine when accompanied by silica. The presence of this body in a plant, besides greatly complicating the investigation, rendered the employment of platina vessels essential, and thus limited the amount of material which could be subjected to examination, besides making it difficult or impossible to observe the progress of an analysis.

The author then stated, that, in the course of some recent investigations into the presence of fluorine in siliceous rocks, he had succeeded in devising a process which was also applicable to plants, and could be carried on in the ordinary glass vessels of the laboratory. The process in the case of plants was as follows:—The plant under examination was burned to ashes as completely as possible. The ashes were then mixed in the cold with oil of vitriol, so as to secure the decomposition of the salts of volatile acids present. The mixture was then transferred to a retort, or flask, provided with a bent tube dipping into water, and the liquid raised to the boiling-point, when fluorine, if present, was evolved in combination with the silicon of the silica, as the gaseous fluoride of silicon, which dissolved in the water with separation of some gelatinous silica. The resulting solution was neutralized with ammonia and evaporated to complete dryness, when the whole of the silicon passed into the condition of insoluble silica, and water dissolved the fluoride of ammonium. The solution of this fluoride could then be dried up and moistened with sulphuric acid, when hydrofluoric acid was evolved, which might be made permanently to record its presence by causing it to etch glass in the usual way. The author has in the meanwhile applied this process almost solely to the stems and trunks of plants, especially to those containing silica, reserving for subsequent investigation their other organs, espe-

cially their seeds and fruits. The following were the results obtained:—

Table of Plants examined for Fluorine. The numbers represent grains of ashes, except in the case of Tabasheer and Wood Opal. The blanks imply that the weight was not known:—

Ashes in grains.	Name of plant.	
200	*Equisetum limosum*	Distinct etching.
	Bambusa arundinacea	Ditto.
	Charcoal (derived chiefly from Oak, and to a smaller extent from Birch)	Ditto.
	Coal	Ditto.
	Barley straw	Ditto.
	Hay (Ryegrass)	Ditto.
35	*Equisetum variegatum*	Faint etching.
19	——— *hyemale*	Ditto.
255	——— *palustre*	Ditto.
	Dactylis cæspitosa	Ditto.
99	*Elymus arenarius*	Ditto.
495	*Saccharum officinarum*	Ditto.
1040	African Teak	Ditto.
	Smilax latifolia	No etching.
	Rosmarinus officinalis	Ditto.
235	*Bambusa Nepalensis*	Ditto.
	Polypodium vulgare	Ditto.
537	Tree Fern	Ditto.
24	*Phalaris arundinacea*	Ditto.
240	Malacca Cane	Ditto.
50	Cocoa-nut shell	Ditto.
127	*Tectona grandis*	Ditto.
80	Tabasheer	Ditto.
1680	Wood Opal	Ditto.

On this table the author remarked, that the siliceous stems which he had found to abound most in fluorine, were exactly those which contained most silica. In particular, deep etchings were procured from the Equisetaceæ and from the Gramineæ, especially the common Bamboo. The last was known to contain silica in such abundance that it collected within the joints in white masses, nearly pure, and had long, under the name of Tabasheer, been an object of interest to natural philosophers. The horse-tails were scarcely less remarkable for the amount of silica contained in their stems, which had led to the employment of one of them (*Equisetum hyemale*) in polishing wood and metals. The African Teak, which like the Bamboo is known sometimes to secrete silica, was also found to contain fluorine, though much less largely than the plants named; whilst the strongly siliceous stems of Barley and Ryegrass also yielded the element in marked quantity. The Sugar-cane, however, gave less striking results than might have been expected, and the same remark applied to the Malacca-cane. Two specimens of silicified wood and one of Tabasheer gave no evidence of the presence of fluorine. So far, however, as the

plants named in the preceding table are concerned, the author does not wish it to be inferred from the negative results which are detailed, that the plants in question are totally devoid of fluorine. With larger quantities of their ashes, positive results would, in all probability, be obtained.

The author's general conclusions were as follows:—1st, that fluorine occurs in a large number of plants; 2nd, that it occurs in marked quantity in the siliceous stems of the Gramineæ and Equisetaceæ; 3rd, that the quantity present is in all cases very small; for although exact quantitative results were not obtained, it is well known that a fraction of a grain of fluoride will yield with oil of vitriol a quantity of hydrofluoric acid sufficient to etch glass deeply, so that the proportion of fluorine present, even in the plant-ashes which contain it most abundantly, does not probably amount to more than a fraction per cent. of their weight. The proportion of fluorine appears to be variable, for different specimens of the same plant did not yield concordant results.

In this, however, there is nothing anomalous, for some Bamboos yield *Tabasheer* largely, whilst others are found to contain none. It seems not unlikely that soluble fluorides ascending the siliceous stem of a plant, on their way to the seeds or fruits in which they finally accumulate, may be arrested by the silica, and converted into insoluble fluosilicates (fluorides of silicon and of a metal); and a Bamboo, for example, secreting Tabasheer, may effect this change where one less rich in silica cannot determine it. The slow or quick drying of a stem may also affect the fixation of fluorides in the stems or trunks of plants.

The sources of the fluorine found in plants may be regarded as preeminently two,—1st, simple fluorides, such as that of calcium, which are soluble in water, and through this medium are carried into the tissues of plants; and 2nd, compounds of fluorides with other salts, of which the most important is probably the combination of phosphate of lime with fluoride of calcium. This occurs in the mineral kingdom in apatite and phosphorite, and in the animal kingdom in bones, shells and corals, as well as in blood, milk, and other fluids.

A recent discovery of the author, communicated to the Royal Society of Edinburgh, has shown that fluorides are much more widely distributed than is generally imagined, and that the trap rocks near Edinburgh, and in the neighbourhood of the Clyde, as well as the granites of Aberdeenshire, and the ashes of coal, contain fluorides, so that the soils resulting from the disintegration of those rocks cannot fail to possess fluorides also. All plants accordingly may be expected to exhibit evidence of their presence in the following portions of their tissues or fluids:—

1. In the ascending sap, simple fluorides.
2. In the descending sap, in association with the albuminous vegetable principles, and in the seeds or fruits, in a similar state of association, fluorides along with phosphates.
3. In the stems, especially when siliceous and hardened, fluorides in combination with silica. The investigation is still in progress.